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High-Pressure Kinetic Evidence for an Associative–Dissociative Changeover for Solvent Exchange Mechanism on the Divalent Metal Ions along the First-Row Transition Metals[1]

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Abstract: The effect of pressure (up to 200 MPa) on the methanol exchange on $[Mn(CH_3OH)_6](ClO_4)_2$ and $[Fe(CH_3OH)_6](ClO_4)_2$ has been studied utilizing ^1H FT NMR T_2 measurements. The derived volumes of activation, ΔV^* in cm^3 mol^{-1}, together with the previously published values for methanol exchange on cobalt(II) and nickel(II) (-5.0 ± 0.2 (Mn^{2+}), $+0.4 \pm 0.3$ (Fe^{2+}), $+8.9 \pm 0.3$ (Co^{2+}), and $+11.4 \pm 0.6$ (Ni^{2+})), give evidence for an associative–dissociative mechanistic changeover for solvent exchange along the first-row transition metals. This is in disagreement with the general belief that substitution reactions on all divalent ions occur via a dissociative activation mode.

Introduction

Simple substitution reactions on divalent cations of the first-row transition metals are generally thought to have a dissociative activation mode. Such a behavior has been clearly established by Eigen and Wilkins for complex formation reactions on Ni(II) and has then been further extended to the other divalent metal ions.[3,4] The exchange of solvent molecules between the primary solvation shell of a cation and bulk solvent may therefore be considered a fundamental reaction for metal ions in solutions. Since one cannot vary the concentration of free solvent nor change the nature of the incoming "ligand", clues to establish the mechanism of solvent exchange are given mainly by the activation parameters. Unfortunately, activation enthalpies and entropies obtained from NMR studies are prone to large nonrandom errors, particularly for paramagnetic ions.[5,6] Even though studying the variation of rates with pressure is technically difficult, the volume of activation, ΔV^*,

$$\Delta V^* = -RT\left(\frac{\partial \ln k}{\partial P}\right)_T \qquad (1)$$

has proved to be extremely useful in the diagnosis of reaction mechanisms.[7,8] It has been observed that random and nonrandom errors in the determination of the rate constants affect ΔV^* less than ΔS^* when similar experimental approaches are used.[6,9] If, as for solvent exchange, there is no charge separation or cancellation on going from the reactants to the transition state, a positive ΔV^* can be directly related to a dissociative activation mode and a negative ΔV^* to an associative process.[10]

We have applied high-pressure NMR to investigate nonaqueous solvent exchange. In a previous paper[10] we reported volumes of activation for *N*,*N*-dimethylformamide, acetoni-

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trile, and methanol exchange on Ni(II) and Co(II). Their values suggested a dissociative interchange (I_d) mechanism for solvent exchange on both ions, Co(II), however, exhibiting less dissociative character. To see whether this trend to less dissociative behavior extends toward the earlier members of the first-row transition metal ions, we examine in this paper the methanol exchange on Fe(II) and Mn(II).

Experimental Section

Dry $[Fe(CH_3OH)_6](ClO_4)_2$ and $[Mn(CH_3OH)_6](ClO_4)_2$ were prepared from the hexahydrated salt and methyl orthoformate using van Leeuwen's procedure.[11] The metal content of the crystalline products was checked by EDTA titration. The water content of the complexes, as determined by Karl-Fischer titration, was less than 0.05 mol of water per mol of salt.

Solutions for NMR study were prepared by weight in a glovebox (water < 2 ppm, oxygen < 5 ppm). Methanol (Fluka puriss. p.a.) was dried with anhydrous calcium sulfate (water content by Karl-Fischer titration less than 50 ppm). Me_4Si (1% by weight) was added as internal line-width standard.

^1H FT NMR spectra were obtained on a Bruker WP-60 spectrometer operating at 60 MHz. T_2 measurements were obtained from the full width at half height of the NMR absorption resonance, $\Delta\nu_{1/2}$ in hertz, by means of the relationship $(T_2)^{-1} = \pi(\Delta\nu_{1/2} - \Delta\nu_{1/2}(Me_4Si))$ where $\Delta\nu_{1/2}(Me_4Si)$ represents the correction for magnet inhomogeneity and external lock instability (the full width at half height of the Me_4Si absorption resonance was typically 2–6 Hz and always less than 20% of $\Delta\nu_{1/2}$). Paramagnetic broadening of the internal Me_4Si could be neglected.

The high-pressure NMR probe used was the same as described previously[12,13] with the addition of an external fluorine lock. The temperature was measured inside the pressure vessel with a 100-Ω platinum resistor[14] and its stability over periods of several hours was better than ±0.1 K.

Data Treatment and Results

Both iron(II) and manganese(II) studies have been performed in the slow exchange region where the exchange rate constant can be obtained from the simplified Swift and Connick equation taking into account a possible outer-sphere interaction:[6,15]

$$\frac{1}{T_{2r}} = \frac{1}{P_m}\left(\frac{1}{T_2} - \frac{1}{T^0_{2A}}\right) = \frac{1}{\tau_m} + \frac{1}{T_{2os}} \tag{2}$$

where T_2 is the observed relaxation time, T^0_{2A} is the relaxation time of the pure solvent ($(T^0_{2A})^{-1}$ for these systems can be neglected with respect to the measured $(T_2)^{-1}$), P_m is the mole fraction of bound solvent, and T_{2os} represents the outer-sphere contribution. τ_m is the residence time of a bound solvent molecule and can be related to the pseudo-first-order reaction rate constant for the solvent exchange by the relationship $k = 1/\tau_m$. It has been clearly demonstrated[6] that this simplified equation yields reliable ΔV^* values in the slow exchange region, despite the fact that it should not be used to obtain ΔH^* and ΔS^*.

The experiments were performed twice at closely similar temperatures. The data for each ion were analyzed according to the method described in a previous paper.[10] The basic relationship between ln k and P is repeated here for easier reference:

$$\ln k = \ln k_0 - \Delta V^*_0 P/RT + \Delta\beta^* P^2/2RT \tag{3}$$

The parameters adjusted were k_0, the zero pressure rate constant, ΔV^*_0, the zero pressure volume of activation, and $\Delta\beta^*$, the pressure-independent compressibility of activation. ΔV^* will refer to the volume of activation obtained assuming $\Delta\beta^* = 0$.

$[Fe(CH_3OH)_6](ClO_4)_2$ in CH_3OH. Variable-temperature ^1H T_2 measurements on the CH_3 protons of free methanol by Breivogel[16] show that a convenient temperature to perform the variable-pressure experiments is ~250 K. This temperature is in the middle of the slow-exchange region, where we have previously shown that eq 1 may be used with little error. Breivogel's study further shows no significant outer-sphere contribution. The rate constants k were thus obtained from eq 4 derived from eq 2 with $(T_{2os})^{-1} = 0$:

$$1/T_{2r} = k \tag{4}$$

The observed rate constants as a function of pressure are given in Table I together with the experimental conditions and the derived volumes and compressibility of activation. Even though no Fe^{3+} was found during analysis of the complex, small amounts of the oxidized species would not affect significantly the volume of activation for Fe^{2+} since, at the temperature used, methanol exchange is very slow for Fe^{3+}.[16]

Table I. Observed Rate Constants for the Exchange of CH_3OH on $[Fe(CH_3OH)_6](ClO_4)_2$ as a Function of Pressure and Derived Volumes of Activation[a,b]

experiment 1, T = 250 K, P_m = 0.079 17		experiment 2, T = 260 K, P_m = 0.029 19	
P, MPa	k, s^{-1}	P, MPa	k, s^{-1}
0.1	1040	0.1	1841
0.1	1079	60.0	1739
25.0	1012	120.0	1604
50.0	1019	200.0	1706
75.0	1021	160.0	1706
100.0	960	90.0	1721
125.0	1000	30.0	1797
150.0	1054	0.1	1765
175.0	1058	45.0	1916
200.0	1063	130.0	1781
95.0	975		
0.1	1042		

$\Delta V^* = +0.4 \pm 0.3$ cm^3 mol^{-1}

$\Delta V^*_0 = +2.1 \pm 0.9$ cm^3 mol^{-1}

$\Delta\beta^* = +(1.9 \pm 0.9)10^{-2}$ cm^3 mol^{-1} MPa^{-1}

[a] Errors quoted are standard deviations. [b] Data are given in the order in which they have been obtained.

$[Mn(CH_3OH)_6](ClO_4)_2$ in CH_3OH. Variable-temperature ^1H T_2 measurements on the OH groups of the free methanol by Breivogel[16] show a well-defined slow-exchange region between 250 and 312 K. For the CH_3 protons there is no region where one of the limiting Swift and Connick equations is valid. Breivogel has shown that the OH and CH_3 protons exchange at the same rate. We are therefore allowed to perform our kinetic study on the OH resonance. At 279 K we are in the middle of the OH slow-exchange region and the outer-sphere contribution at that temperature (obtained by extrapolation of the low-temperature relaxation rates where chemical exchange no longer affects $(T_{2r})^{-1}$ significantly) represents less than 1% of the observed relaxation rate. $(T_{2os})^{-1}$ can thus be neglected and the exchange rates were obtained through eq 4. The observed rate constants as a function of pressure are given in Table II together with the experimental conditions and the derived volumes and compressibility of activation.

Discussion

It is conventional to discuss the mechanism of ligand substitution reactions in terms of the classification of Langford and Gray.[17] Since much of the ensuing discussion involves the use of this classification, it is convenient to review their ideas first. Their approach is operational and depends on kinetic tests that may be applied. Thus if a mechanistic test is able to detect the presence of an intermediate of increased or decreased coordination number the mechanism is assigned as associative (A) or dissociative (D) respectively. Otherwise, it is assigned as an interchange (I) process. This last class is subdivided into two groups: associative interchange (I_a), when there are im-

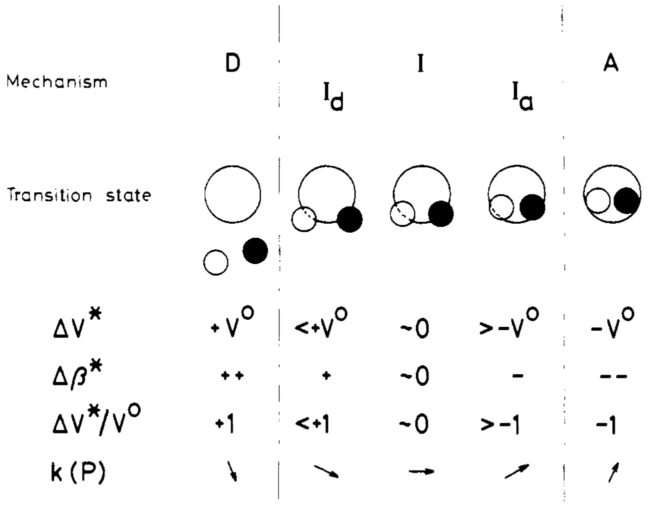

Figure 1. Schematic representation of solvent exchange transition states for various mechanisms and associated values of variable pressure activation parameters. The large circles represent the limit of the first solvation sphere; the metal ion and the five nonexchanging solvent molecules are not shown. The small shaded and unshaded circles represent the entering and leaving molecule. V^0 is the solvent molar volume. This representation is not meant to imply a particular geometry of the transition state.

Table II. Observed Rate Constants for the Exchange of CH_3OH on $[Mn(CH_3OH)_6](ClO_4)_2$ as a Function of Pressure and Derived Volumes of Activation[a,b]

experiment 1, T = 279 K, P_m = 1.348 × 10^{-4}		experiment 2, T = 279 K, P_m = 1.348 × 10^{-4}	
P, MPa	$10^{-5}k$, s^{-1}	P, MPa	$10^{-5}k$, s^{-1}
0.1	2.540	0.1	2.494
30.0	2.844	40.0	2.898
60.0	3.004	80.0	3.203
90.0	3.216	125.0	3.320
120.0	3.425	174.5	3.819
150.0	3.651	220.0	4.117
210.0	4.056	200.0	3.912
181.0	3.789	150.0	3.529
105.0	3.330	100.0	3.261
0.1	2.532	59.5	2.971
		20.0	2.821
		0.1	2.504

$\Delta V^* = -5.0 \pm 0.2$ cm^3 mol^{-1}
$\Delta V^*_0 = -6.5 \pm 0.5$ cm^3 mol^{-1}
$\Delta\beta^* = -(1.5 \pm 0.5)10^{-2}$ cm^3 mol^{-1} MPa^{-1}

[a] Errors given are standard deviations. [b] Data are given in the order in which they have been obtained.

portant entering groups effects, or dissociative interchange (I_d), when there are not.

For solvent exchanges, several important points arise with regard to this classification. Firstly, as discussed in an earlier paper,[10] there are very few kinetic tests that may be applied and recourse has to be made to the comparison of activation parameters. In this regard, the volume of activation is of supreme importance. Swaddle[18] has discussed why, for solvent exchange reactions, the sign of ΔV^* is immediately diagnostic of the activation mode. Secondly, the symmetrical nature of solvent exchange imposes certain restrictions on the nature of the reaction coordinate and the structure of transition states and reactive intermediates. Thus, obviously, the reaction coordinate must be symmetrical to the reverse reaction. For an A mechanism where there is a reactive intermediate of increased coordination number and hence two transition states, they must necessarily have identical structures. Similar arguments apply to a D mechanism also. For an interchange mechanism where there is no reactive intermediate, symmetry arguments require that, at the transition state, bonding to both entering and leaving solvent molecules must be identical. Thus for an I_d mechanism, where there is little bonding to the entering group, there must of necessity be little bonding to the leaving group. Conversely, for an I_a mechanism, both entering and leaving groups must have considerable bonding to the metal. From a structural viewpoint, the only difference between I_d and I_a mechanisms for solvent exchange is the degree of expansion of the transition state. The volume of activation, the difference between the volumes of transition state and reactants, can thus yield a direct measure of this expansion and hence of the dissociativity of a reaction. As discussed in various papers,[2,7,10] ΔV^* for D and A mechanisms tend toward plus and minus the solvent partial molar volume V^0. The quantity $\Delta V^*/V^0$ can therefore be used for mechanistic evaluation of solvent exchange. Moreover, intermediate values of this quantity are indicative of interchange processes, being positive for I_d and negative for I_a mechanisms. For ligand substitution reactions, Langford and Gray[17] defined the subdivision between I_a and I_d in terms of the existence or absence of important entering-group effects. For solvent exchange, such criteria cannot be applied. However, as shown above, one may envisage a continuous spectrum of transition states characterized by their degree of expansion ranging from highly associative to highly dissociative. For convenience, we shall arbitrarily define, for solvent exchange, the changeover of mechanism to occur when ΔV^* equals zero. Figure 1 shows a schematic representation of the transition states for the various mechanisms together with their expected variable-pressure activation parameters.

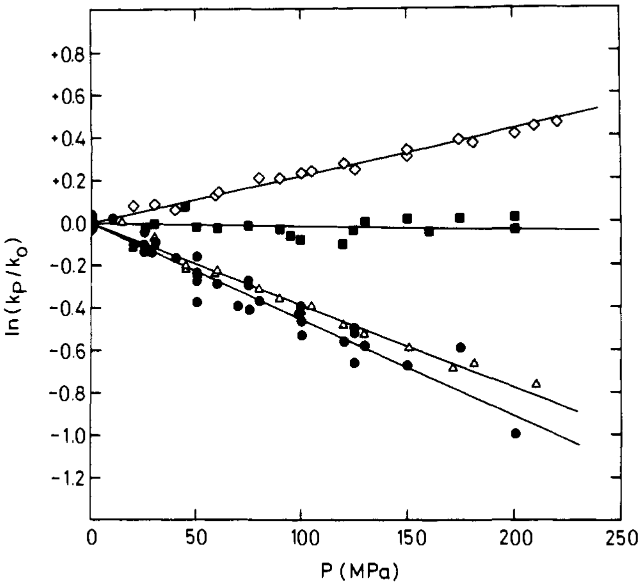

Figure 2. Experimental and calculated values of ln (k_P/k_0) as a function of pressure for methanol exchange on Ni(II), Co(II), Fe(II), and Mn(II): ●, Ni(II), 307 K; △, Co(II), 279 K; ■, Fe(II), 255 K; ◇, Mn(II), 279 K.

Figure 2 shows the variation of rate constant with pressure for the methanol exchange reactions on Mn^{2+} and Fe^{2+} together with the results for Co^{2+} and Ni^{2+} reported earlier[10] and Table III gives the derived activation parameters. For each of the reactions, the low values of $\Delta V^*/V^0$ are clearly in accord with an interchange process. These assignments are borne out[7] by the extremely small values of $\Delta\beta^*$, positive for the three dissociative interchanges and negative for the associative interchange. Since these values are negligible within experimental error, we shall restrict our discussion at present to the linear results assuming $\Delta\beta^*$ equals zero.

Table III. Activation Parameters for Methanol Exchange on Nickel(II), Cobalt(II), Iron(II), and Manganese(II) Perchlorates

	ΔG^*_{298}, kJ mol^{-1}	ΔH^*, kJ mol^{-1}	ΔS^*, J K^{-1} mol^{-1}	ΔV^*, cm^3 mol^{-1} [a]	$10^{-2}\Delta\beta^*$, cm^3 mol^{-1} MPa^{-1}	$\Delta V^*/V^0$ [b]
Ni^{2+}	55.9[c]	66.1[c]	+33.5[c]	+11.4 (307 K)[d]	+2.0	+0.28
Co^{2+}	48.7[c]	57.7[c]	+30.1[c]	+8.9 (279 K)[d]	+2.0	+0.22
Fe^{2+}	46.2[e]	50.2[e]	+12.6[e]	+0.4 (255 K)[f]	+1.9	+0.01
Mn^{2+}	41.2[e]	25.9[e]	−50.2[e]	−5.0 (279 K)[f]	−1.5	−0.12

[a] Temperature given in parentheses. [b] V^0, the molar volume of methanol, was obtained from density data at the temperature of the ΔV^* measurement. [c] Luz, Z.; Meiboom, S. *J. Chem. Phys.* **1964**, *40*, 2686-2692. [d] Reference 9. [e] Reference 15. [f] This work.

Table IV. Crystal Field Activation Energies for D and A Transition States for Divalent High-Spin First-Row Transition Hexaaquo Metal Ions (ρ = 1)

		D mechanism		A mechanism	
	Dq/cm^{-1} [a]	CFAE/*Dq*	CFAE/kJ mol^{-1} [b]	CFAE/*Dq*	CFAE/kJ mol^{-1} [b]
d^0		0	0	0	0
d^1		+0.286		−0.857	
d^2		+0.572		−1.714	
d^3	1230	+2.0	+29.3	+4.25	+62.3
d^4	1410	−1.428	−24.0	+0.214	+3.6
d^5	850	0	0	0	0
d^6	1000	+0.286	+3.4	−0.857	−10.2
d^7	930	+0.572	+6.3	−1.714	−19.0
d^8	890	+2.0	+21.2	+4.25	+45.1
d^9	1200	−1.428	−20.4	+0.214	+3.1
d^{10}		0	0	0	0

[a] Reference 4, p 76. [b] 1000 cm^{-1} ≡ 11.9 kJ mol^{-1}.

The most interesting point in these results is that there is a gradual change of sign of ΔV^* going across the series; nickel(II), as discussed before,[10] with its positive value is clearly showing dissociative d behavior whereas manganese(II) is clearly showing some associative a character. Iron(II) may be regarded as reacting by a pure interchange I mechanism since values of k show almost negligible change with pressure.

The other activation parameter frequently used for mechanistic evaluation is ΔS^*. Unlike ΔV^*, which is more easily understood conceptually in terms of (possibly naive) changes of bond lengths effecting partial molar volumes of reactants and transition state, the entropy of activation is much more difficult to appreciate conceptually. However, for closely related reactions one may suppose ΔS^* to be related to an "increase in randomness"[18] between reactants and transition state. It is thus gratifying to note that, in spite of the very large errors frequently found in NMR-derived ΔS^*, the trend toward associative behavior is mirrored by the entropies available in the literature.

It has been suggested that a correlation should exist between ΔV^* and ΔS^*. While there is no necessary thermodynamic relationship between the two, we might expect some form of relation between the degree of expansion of a transition state and its randomness. A reasonable linear relation between ΔS^* and ΔV^* for the acid aquation of some nonlabile transition-metal complexes has been noted by Twigg.[19] More recently, Lawrence and Suvachittanont[20] have studied the isomerization reactions of inert octahedral complexes in solution. They use the fact that, for some of these reactions, a ΔV^* vs. ΔS^* correlation is obtained, and for the others, no such correlation is observed as evidence for two distinct mechanisms operating. The correlation is observed for the reactions thought to be occurring via a bond-making or -breaking mechanism whereas small ΔV^* and large negative ΔS^* values are thought to arise for those occurring via twist mechanisms.

The reactivities of octahedral transition metal ions toward substitution are frequently discussed in terms of crystal field theory. Thus, for example, Basolo and Pearson[21] calculated the change in crystal field stabilization energy between octahedral → square pyramidal, octahedral → pentagonal bipyramidal, and octahedral → octahedral wedge corresponding to D, A, and I reactions, respectively, for both high- and low-spin states. These crystal field activation energies (CFAE) readily explain the general trends in lability of metal ions of the transition series, but the labilities were all equally well explained by all three mechanistic models. Thus, CFAEs could not in general aid in mechanistic prediction for octahedral systems. The calculation of crystal field stabilization energies for any symmetry below octahedral requires the ratio of a certain electron repulsion integral ρ which in general is not known. Treating ρ as an unknown, Companion[22] has been able to explain quantitatively the variation of water exchange activation energies for the divalent first-row transition-metal ions assuming a D mechanism. It has since been shown[23] that the optimum value of ρ obtained by Companion, slightly less than 1, is much more reasonable than the value of 2 adopted by Basolo and Pearson. In Table IV we give the results of CFAE calculations for both D and A mechanisms for ρ = 1 using the one-electron formulae of Spees, Jayarama, Perumareddi, and Adamson.[24] The *Dq* values refer to water since values are not readily available for CH_3OH. However, the *Dq* value for Ni^{2+} in methanol (850 cm^{-1}) is very close to that of water (860 or 890 cm^{-1})[25] and similar behavior should be expected for the other ions. It had been hoped that Table IV would show a progressive lowering of the activation energy of the A mechanism relative to the D mechanism on going to the earlier members of the series but this is clearly not so. The table suggests that Co^{2+} should be most associative followed by Fe^{2+}, then Mn^{2+}, and with Ni^{2+} most dissociative.

For an octahedral complex, in the absence of π bonding, the t_{2g} orbitals are nonbonding and the e_g orbitals σ antibonding. The e_g orbitals never change their occupancy from Mn^{2+} to Ni^{2+} and the tendency toward less and less associative behavior seems to be related to the occupancy of the t_{2g} orbitals. These orbitals, being nonbonding, do not point toward the ligands but instead point between adjacent ligands. Naively, one may suppose that increased occupancy of these orbitals makes the approach of a seventh solvent toward the face of the octahedron less and less electrostatically favorable. Such a behavior is observed for the nonlabile trivalent metal ions where chromium(III) t_{2g}^3 is known to react via an I_a mechanism but low-spin cobalt(III) t_{2g}^6 reacts via an I_d mechanism.[7] Similarly, substitution reactions of the low-spin iron(II) complex $[Fe(CN)_5(3,5\text{-}Me_2\text{-}py)]^{3-}$ t_{2g}^6 with a variety of charged and uncharged ligands are known to occur via a D mechanism[26] with ΔV^* values between +20.3 and +21.2 cm^3 mol^{-1}. The above arguments concerning the occupancy of the t_{2g} orbitals neglect the changes in degeneracy of the d electrons caused by the altered symmetry of the ligand field at the transition state. This is precisely the effect that CFAE attempts to take into account.

It is generally believed that associative behavior may be the norm for trivalent transition metal ions with low-spin cobalt(III) reacting dissociatively due to its very small size[18] (r = 0.53 Å).[27] The ionic radii of Mn^{2+} (0.82 Å), Fe^{2+} (0.77 Å), Co^{2+} (0.74 Å), and Ni^{2+} (0.70 Å) are in accord with the argument that the larger ions react more associatively. The extremely small size of low-spin iron(II) (0.61 Å) is in accord with its highly dissociative behavior. The trivalent ions are smaller than the divalent ions and we should suppose the size effect to be of greater importance in this latter case. For example, it has been shown that the ΔV^* values for water and DMF exchange on $M(NH_3)_5S^{3+}$ are decreasing from cobalt to rhodium and iridium.[18,28]

We have shown on the basis of ΔV^* values a mechanistic changeover for the solvent exchange in methanol on going from Mn^{2+} to Ni^{2+}. Moreover, we have previously shown that, for the nonaqueous solvents methanol, DMF, and acetonitrile, the effect of change of solvent on $\Delta V^*/V^0$ for exchange on Ni^{2+} and Co^{2+} is very small.[10] Recently, a value of ΔV^* of +7.1 cm^3 mol^{-1} has been obtained for water exchange on Ni^{2+} using ^{17}O NMR.[29] We are thus confident that the mechanistic changeover will also occur in other solvents.

For the trivalent ions, evidence is slowly accumulating that the early members of the first transition series such as Ti^{3+} and V^{3+} may also react by associative mechanisms.[30] The associative behavior of Cr^{3+} and the dissociative behavior of Co^{3+} thus lead us to the conclusion that a similar trend toward associativity for the earlier members may occur for both divalent and trivalent ions.

The assumption that all divalent transition metal ions react dissociatively is certainly proved for Ni^{2+} and Co^{2+} where there is an absolute wealth of evidence. However, for Fe^{2+} and Mn^{2+}, the evidence on which the I_d postulate has been built is much less firm owing to the extremely small number of complex formation reactions studied.[30] Our assignment of an associative activation mode for Mn^{2+} is highly controversial but the data on which the assignment is based are such that they are impossible to interpret in any other way. We are thus forced to conclude that, *for the first-row transition-metal ions, only the later members substitute via an I_d mechanism, while the earlier members show associative I_a behavior, with the changeover occurring around Fe(II) for the divalent ions.* High-pressure ^{17}O NMR measurements are in progress to confirm experimentally this trend in water.

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References and Notes

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